



Special Spherical Shell-shaped Foam deriving from Guanidine Phosphate – Pentaerythritol system and its Intumescent Fire Retardant effects on Polypropylene



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ABSTRACT

An intumescent fire retardant (IFR) system based on guanidine phosphate (GP) and pentaerythritol (PER) was proposed. Decomposition products of GP were studied by thermogravimetric analysis (TGA) combined with pyrolysis gas chromatography-mass spectrometry (Pyrolysis GC–MS) at first. The pure intumescent fire retardant (IFR) GP-PER was studied then. When the IFR was combusted, the special spherical shell-shaped foam was generated. The foam was made up of soluble phosphorus degradation products (PDPs) and insoluble nitrogenous - carbonaceous char consisting of fused ring and heterocyclic ring structures derived from the degradation products of pentaerythritol phosphate esters and condensed cyanamide derivatives. Scanning electron microscopy (SEM) and Raman spectroscopy as well as ion chromatography (IC) and elemental analysis were used to study the morphology and the moieties of the foam. The mechanism of the special foam formation was proposed with the help of TGA results in the paper. Eventually, mixtures of this IFR blended in polypropylene (PP) matrix were prepared and the fire retardancy was studied. Fourier transform infrared spectroscopy (FTIR) indicated the variation of the foam moieties from 270 °C to 500 °C. Experiments proved the optimal mass ratio of GP and PER is 2:1 to get fire retardancy in PP matrix. With an addition of 25 wt%, the limited oxygen index (LOI) could reach 31% and vertical burning ratings (UL-94 tests) reach a V-0 rating.

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1. Introduction

Intumescent fire retardant (IFR) is a halogen-free green product to solve the problems of corrosiveness, toxicity, etc. caused by the combustion products coming from the halogenated fire retardants [1]. Generally, the IFR formulations comprise three elements: acting as a carbon rich polyol compound (glycerol, PER, etc.), acid source (phosphates, sulfates, etc.) and blowing agents. The carbon rich polyol and acid react to form the esters which undergo pyrolysis and carbonization at high temperature. The blowing agents help swell the generated carbonaceous melt into the foam [2].

As the environmental friendly IFR systems are attracting more and more attention, for PP, the widely used intumescent fire retardant-APP and PER system has been studied by scientists all over the world for the past few decades. Guanidine phosphate, however, was once used for treatment to gain fire retardancy in

woods [3] and fibers [4]. Bourbigot et al. found that when the cotton fabric was treated with formulations based on guanidine dihydrogen phosphate or diguanidine hydrogen phosphate, the LOI could reach 31% [5]. And the concept of the “intumescent fire retardant treatments” for flexible materials was stated later in 2007 [6]. In fact, the treated flexible material could be considered as an “intumescent fire retardant” system: the fiber or wood matrix acts as a macromolecular carbon source, GP works as acid source and blowing agents. Nevertheless, there is almost no report of GP blended with small molecular carbon source, such as PER, glycerin or sorbitol, to be an IFR system.

A preliminary research was done on GP-PER system and we were surprised to obtain higher LOI values than in the APP-PER system in PP matrix. Although GP is much more water soluble than APP which makes itself harder to be industrialized, this paper aims at ascertaining the thermal decomposition of GP, the different foam structure formed by GP-PER as well as the mechanism of the foam formation and the intumescent fire retardant effects of the GP-PER system on PP matrix. Therefore, deep investigation on this GP-PER system was done in this work.

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The thermal decomposition process of GP was explained by TGA combined with Pyrolysis GC–MS. The thermal behavior of the GP-PER system was also investigated by TGA. Special spherical shell-shaped foams were obtained and observed both by digital pictures and SEM images. IC and elemental analysis were used to analyze the composition of formed foams: the soluble moieties phosphorus degradation products (PDP_S), insoluble nitrogenous-carbonaceous char derived from the degradation products of pentaerythritol phosphate esters and condensed cyanamide derivatives. The mechanism of the foam formation was proposed then based on the above analysis. Eventually, mixtures of PP blended with 25 wt% GP-PER (IFR1) were prepared, and the fire retardancy was compared with the classic APP-PER (IFR2) system via LOI and UL-94 tests.

2. Experimental

2.1. Materials

Polypropylene (F280Z, China Petroleum & Chemical Corporation Zhenhai Refining & Chemical Company, Melting index (MI) = 2.83 g/10 min), pentaerythritol (PER, CP, Shanghai Lingfeng Chemical Reagent Co., China), guanidine phosphate (GP, CP, Aladdin reagent Co., Ltd., China), antioxidant (B215, Suzhou Jixin Commerce Trade Co., Ltd., China), ammonium polyphosphate (APP, $n > 1000$, Crystalline form II, average particle size of 10 μm , Shanghai Xusen Non-Halogen Smoke Suppressing Fire Retardants Co., Ltd., China).

2.2. Sample preparation

GP-PER mixtures and APP-PER composites were placed in crucibles and heated in a muffle furnace at 500 °C for 30 min to obtain the foams. Some of the foams formed by GP-PER were used for digital pictures, and some were for IC and elemental analysis. The cross sections of the foams formed by GP-PER and APP-PER were obtained by cutting longitudinally. The soluble portion of the foam formed by GP-PER was dissolved in deionized water with ultrasonic and sedimentation treatments. The liquid was diluted 10 times for IC analyses. The remaining insoluble portion of the foam was dried for elemental analysis and Raman spectroscopy.

PP/IFR mixtures were prepared in two steps. First, PP, GP-PER (IFR1) and a slight amount (0.2 wt%) of antioxidants were mixed at 180 °C using a mixer (SU70-1, Changzhou Suyan Science and Technology CO., Ltd., China), with a rotation speed of 80 r/m for 7.5 min. The GP-PER ratio was varied from 2:3 to 5:1 (with a dosage of 25 wt%). Then the blended samples were pressed into sheets by compression molding (XQLB-350*350, Shanghai Rubber Machinery Factory) at 180 °C, 5 min for hot molding and 3 mins for cold molding. The same methods were used to obtain PP/APP-PER (IFR2). The sample sheets were further cut into standard specimens for fire retardancy measurements.

2.3. LOI and UL-94 tests

LOI test was performed according to ISO 4589 in a JF-3 oxygen index meter (Jiangning Analytical Instrument Co., Ltd., China). Sample size was $130 \times 6.5 \times 3 \text{ mm}^3$. UL-94 test was performed according to ISO 1210 in a CZF-2 Vertical burning tester (Jiangning Analytical Instrument Co., Ltd., China). Sample size was $125 \times 12.5 \times 3 \text{ mm}^3$.

2.4. Thermogravimetric analysis

Thermogravimetric analysis was performed at a heating rate of 10 °C/min, under nitrogen atmosphere, from ambient to 600 °C,

using an STA-409 thermal analyzer (Netzsch Co., Ltd., Germany). The weight of samples was about 10 mg.

2.5. Pyrolysis gas chromatography-mass spectrometry (pyrolysis GC–MS)

A Thermal Cracker (Pyroprobe 5000, CDS, US) was used to collect the pyrolysis products of GP at different steps of thermal decomposition and an MS Spectrometer (GC7890A and MSD 5975C, Agilent Technologies Co., Ltd., US) was used to investigate the products. The collecting temperatures were 80 °C, 275 °C, 300 °C and 418 °C, which respectively corresponded to the stages of TGA analysis. The MS Spectrometer adopted NIST library system to detect with an operating range of 14–550 amu. The probe used electron impact mode, with the electron energy of 70 eV. The pyrolysis products were separated with HP-5MS column in a helium flow of 1 ml/min.

2.6. Composition and property of the spherical shell-shaped foams

IC analyses were applied to detect the concentration of PO_4^{3-} and NH_4^+ in the hydrolyzed soluble moieties of foam using an ICS-2000 system (Dionex Co., Ltd., USA). The pure IFR was heated in a muffle furnace at 500 °C for 30 min. The soluble portion of the foam was dissolved in deionized water with ultrasonic and sedimentation treatments. The liquid was diluted 10 times for IC analyses.

Elemental analysis was used to study the elemental composition of the insoluble portion of the special foam using a Vario EL III (Elementar Analysensysteme GmbH, Germany). Remaining insoluble portion of foam was dried. The weight of the sample was about 10 mg.

Raman spectroscopy was used to characterize the degree of order of char in the insoluble portion of the foam using an in-Via-reflex (Renishaw, UK), under nitrogen atmosphere, at ambient temperature. The laser wavelength is 514.5 nm with the Raman shifts from 800 to 3000 cm^{-1} . The integrated intensity ratio of the band D and G was used to manifest the “degree of order of char”, $R = I_d/I_g$.

Scanning electron microscopy (SEM) was performed by a JSM-6360 scanning electron microscope (JEOL Co., Ltd., Japan) to observe the morphology of the special spherical shell-shaped foam surface. The IFR mixtures were heated in the muffle furnace at 500 °C for 30 min. The surface layer of foam was selected and was sputter-coated with a gold layer prior to observation. The accelerating voltage was 15 kV.

2.7. Fourier transform infrared spectroscopy

FTIR spectra were recorded with a 5700 spectrometer (Nicolet Co., Ltd., USA). Samples were mixed with KBr powders and compressed into wafers. The resolution is 4 cm^{-1} , the number of scan is 32. Melts of the PP/IFR mixtures were obtained after the heating treatments in a muffle furnace at 270 °C, and 340 °C for 30 min, and the char residues of the PP/IFR mixtures were obtained after the heating treatments in a muffle furnace at 400 °C and 500 °C for 30 min.

3. Results and discussion

3.1. Thermal behavior of GP

3.1.1. TGA of GP

Guanidine phosphate (Guanidine hydrogen phosphate) is a divalent guanidine salt of phosphoric acid. As a resonance hybrid, the double bond C=N and single bond C–N of the guanidine could

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